Carbon in watershed bedrock and its importance in global carbon cycling

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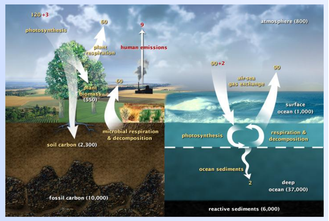
BACKGROUND

- Carbon is a fundamental element for life, and an important component of greenhouse gases in Earth's atmosphere.
- It is thereby of primary interest to Earth scientists to account for the global carbon budget, the balance of exchanges of carbon thru pathways in Earth systems.
- Over geologic timescales, weathering of silicate rocks plays a significant role in the regulation of atmospheric carbon dioxide and thereby global climate.
- My study area is the Sierra de las Minas mountain range of Guatemala. This area is of particular interest because of its steep watersheds which drain tectonically active terrain. The amount of transport of sediment, organic carbon and chemical weathering products is disproportionate to its size, and thereby it is an ideal setting for geochemical analyses.



PURPOSE

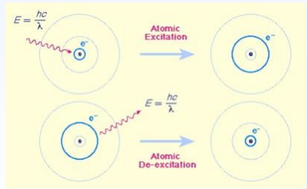
- The purpose of the study is to assess the chemistry of the weatherable rocks in the region, particularly shale, because tectonics and lithology may exert control on annual CO_2 consumption rates due to high silicate weathering.
- To quantify total inorganic carbon (TIC) and organic carbon (TOC) and the bulk elemental composition of shale samples, indicating the potential reservoirs and sources of carbon from minerals and biota
- Contribute to a better understanding of the carbon cycle which involves evaporation into the atmosphere and precipitation onto land.
- Provide insight into silicate weathering of the region, which consumes CO_2 and forms precipitates of $CaCO_3$ that are delivered to the ocean. The reaction results in the net loss of one mole of CO_2 from the atmosphere. This is an important component of the complex dynamics of the chemical equilibrium of the ocean and atmosphere.

MATERIALS AND METHODS

Shale samples which had undergone various degrees of weathering were collected from streambeds and outcrops of watersheds in the study region.

X-Ray Fluorescence Spectrometry

Analysis for major, minor ions and trace elements commonly used in research for geochemistry.
Detection of characteristic wavelength emissions from excited electrons as they return to their ground state following the ionization of the atom.
The spectrometer was calibrated with standards from the USGS and JGS.



Elemental Analysis

The Elemental Analyzer combusts the sample at over 1800 ° C, evolving a carbon dioxide signal that is carried by helium gas to the detector.
The samples were analyzed for carbon prior to and after acidification, allowing for the distinction between organic carbon and carbonate minerals, as the acidification reaction evolves carbon dioxide from the carbonates in the sample.

Loss on Ignition (LOI)

This method has been commonly used to estimate the amount of organic matter and carbonate mineral content of soils, and was utilized herein this study to analyze rocks. Organic matter is completely destroyed after burning at 550 ° C and carbonates are burned off at 950 ° C, allowing for gravimetric analysis of the samples.

STOICHIOMETRY

•When looking at long periods of time, the long-term balance of CO_2 is controlled by the rate of input from volcanic gases and output via silicate weathering, anthropogenic perturbation notwithstanding.

$$CO_2 + H_2O \Leftrightarrow H^+ + HCO_3$$

: Dissolved carbon dioxide reacts with water to produce carbonic acid upon precipitation

•Carbonic acid dissolves calcium-bearing silicates, resulting in the consumption of two moles of CO_2

$$2CO_2 + 3H_2O + CaSiO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4$$

• The freed calcium ions react with bicarbonates (an intermediate in the deprotonation of carbonic acid) and precipitates as $CaCO_3$.

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + H_2O + CO_2$$

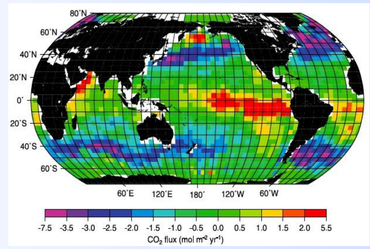
•These reactions demonstrate the interplay of molecules involved in the cycling of carbon from atmosphere to lithosphere.

RESULTS

According to the LOI method
- TOC levels range 1.8-5% and 1-4% for TIC.

The Elemental Analyzer showed to be a more conservative approach to quantifying TOC and TIC.
- TOC levels range 0.12-2.2% and 0-0.5% for TIC.

The Elemental Analyzer had an average percentage error of ~1%.



Simulated average monthly CO_2 exchanges between the ocean and the atmosphere, computed from 41 years of pH and wind speed measurements. The yellow / red boxes correspond to an "upgoing" flux, and the blue / green to a "downgoing" flux. Bordering Central America the net flux is going from the atmosphere to the ocean. (image taken from Dr. Glassman's Journal)

Image of streambed shales taken during sample collection

Left: Dr. Carey standing adjacent to a large shale outcrop.

CONCLUSIONS

The carbonate content of the shale is of particular importance because carbonate weathering provides bicarbonates which directly affect the alkalinity of the stream water, as a high bicarbonate load increases the buffering capacity of the water.
The data add to the overall understanding of factors controlling sediment input to the oceans for a region characterized by high sediment transport disproportionate to land surface area.
The shales were analyzed to understand potential reservoirs of organic matter and carbonate minerals, important in the fluvial flux of carbon and the weathering potential of the lithology.
The analyses provided means for a review of methodologies in quantifying TOC and TIC in rocks.

REFERENCES

1. Goldsmith, Steven T., Anne E. Carey, Brent M. Johnson, Susan A. Welch, W. Berry Lyons, William H. McDowell, and Jeffrey S. Pigott. "Stream Geochemistry, Chemical Weathering and Co2 Consumption Potential of Andesitic Terrains, Dominica, Lesser Antilles." *Geochimica Et Cosmochimica Acta* (2009):
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